



ELECTROLESS COPPER PLATING MACHINE [THEREOF],
AND MULTI-LAYER PRINTED WIRING BOARD

5 BACKGROUND OF THE INVENTION

[1. Field of the Invention]

The present invention relates to ^{an} [An] electroless
copper plating method of reducing the concentration of
byproduct ions and deposition of byproducts in a
10 plating solution, a device thereof, and an application
thereof.

[2. Description of the Prior Art]

^{the} [A] usual electroless copper plating solution
contains copper ions, a copper ion complexing agent, a
15 copper ion reducing agent, and a pH conditioner, which
must be supplied as ^{the} [a] plating advances. However, this
supply increases anions in pairs with copper ions,
oxidant ions of the copper ion reducing agent, and
cations of the pH conditioner in the plating solution.

20 These ions increasing in the plating solution will
deteriorate the physical properties of the plated
layer, particularly the elongation ratio of the plated
layer, reducing the reliability of the plated layer.
Further, ^{this} [it] reduces the stability of the plating
25 solution and causes abnormal deposition and autolysis.

Conventionally, to avoid such problems and ^{to maintain} [keep] a constant salt concentration in the plating solution, various plating ^{techniques} [methods] have been ^{used,} [taken] such as changing plating solutions at short-time intervals, and continuously adding a new plating liquid to the plating solution in use. However, these [methods] ^{approaches} require a large quantity of expensive copper plating solution and a lot of labor and money to dispose of liquid wastes.

Japanese Non-examined Patent Publication No.56-136967 (1981) has disclosed a method of continuously removing such cumulative ions by an electro dialysis. This method requires complicated operations to [keep] ^{maintain} the optimum pH for dialysis. Further, the ion selecting membrane which allows plating blocking ions only to penetrate the membrane is mechanically weak, ^{difficult} [hard] ^{maintain} to [be maintained], and too expensive.

Japanese Non-examined Patent Publication No.7-268638 (1995) has disclosed a plating method characterized by selecting the metallic ion reducing agent and the pH conditioner in the non-electro plating solution so that the oxidant ion of the metallic ion reducing agent and the cation of the pH conditioner may react into an insoluble salt to prevent oxidant ions of said metallic ion reducing

agent from increasing in said plating solution.

However, this method is not effective to prevent^{an} increase of anions in pairs with metallic ions. The increase of the anions will deteriorate the plating characteristics. This method also ^{suggests} [discloses] that the use of copper oxide or copper hydroxide in copper plating will suppress characteristic deterioration of the plating solution. In this case, however, the solubility of ^{the} copper oxide or copper hydroxide has a great influence.

Solid copper oxide or copper hydroxide is usually added to the plating solution. If the solid is not dissolved completely into the plating solution, the particles left undissolved are plated as the cores. This causes abnormal deposition or autolysis. Further, copper oxide and copper hydroxide are more expensive than copper sulfate as copper ion sources, which is conventionally used for copper plating. That's the reason why copper oxide and copper hydroxide have not been put in practical use.

Japanese Non-examined Patent Publication No.7-286279 (1995) has disclosed a method of adding barium hydroxide to the non-electro plating solution and removing excessive sulfuric ions as barium sulfate from the plating solution. However, this method using

formalin (35 % aqueous formaldehyde solution) cannot
[be free from] ^{avoid a consequent} increase of oxidant ions of the copper
ion reducing agent in the copper plating solution. The
oxidant ions of the copper ion reducing agent in this
5 method are formic ions and cannot be removed because
barium formate has too great a solubility to be
precipitated.

Further, this method does not blow air into the
solution while adding barium hydroxide into the
10 plating solution. When alkaline barium hydroxide is
added to the plating solution, the pH value of the
plating solution becomes higher. In electroless
copper plating , the plating solution becomes unstable
when its pH goes too high. Consequently, copper may
15 deposit on unwanted places. This abnormal deposition
on printed circuits and the like may cause short-
circuits, reducing the yield of ^{the} products. Deposition
on the walls of the plating bath may drastically
deteriorate the workability.

20 The conventional plating equipment is usually
designed to directly add copper ions, the copper-ion
reducing agent, and the pH conditioner into the
plating bath. However, this equipment cannot be free
from ^{the} floating of solid particles of insoluble salt in
25 the plating solution. The floating solid particles

when deposited on wiring boards may cause abnormal deposition on the boards.

If such a solid particle is caught in a through-hole on a printed wiring board, it prevents part of the through-hole from being plated, causing^a discontinuity of the wiring (which is termed "through-hole void").

In continuous electroless copper plating, byproduct ions such as anions in pairs with copper ions and oxidant ions of the copper ion reducing agent increase in the plating solution. This increasing^a of the byproduct ions prevent the electroless copper plating reaction from forming normal plating layers and reduces the quality of the plated layer. This not only reduces the mechanical properties of the plated layer, but also causes abnormal deposition of metal on unwanted locations. Up to now, there have been disclosed no effective electroless copper plating method of preventing the increase of plating blocking ions or removing the increased plating blocking ions and refreshing the plating solution.

SUMMARY OF THE INVENYION

The main purpose of the present invention is to

provide a method of removing plating blocking ions such as anions in pairs with copper ions and oxidant ions of the copper ion reducing agent from the electroless copper plating solution and keeping a constant salt concentration in the electroless copper plating solution during plating, a device to realize said method, and applications thereof.

[The]^A summary of the present invention is as follows:

[1] An electroless copper plating method using a plating solution containing copper sulfate as copper ion sources, and a copper ion complex agent, a copper ion reducing agent or glyoxylic acid as a copper ion reducing agent, and pH conditioner, wherein said method comprises steps of using the hydroxide of an alkaline earth metal as said pH conditioner to react with sulfuric ions in the electroless copper plating solution into a salt of said alkaline earth metal, removing the precipitate from the plating solution, measuring at least one of the concentration of sulfuric ion in the plating solution (when the copper ion reducing agent is used) and the concentration of oxalic ion in the plating solution (when glyoxylic acid is used) and keeping an optimum sulfuric ion or oxalic ion concentration or preferentially 0.1 mol per

liter or less of sulfuric ion and 0.2 mol per liter or less of oxalic ion during plating.

[2] An electroless copper plating method using a plating solution containing copper sulfate as copper ion sources, and copper ion complex agent, a copper ion reducing agent or glyoxylic acid as the copper ion reducing agent, and pH conditioner, wherein said method comprises steps of adding at least one of alkaline earth metal, alkaline earth metal oxide, alkaline earth metal hydroxide, and alkaline earth metal salt (excluding sulfuric salt) to the plating solution to react with sulfuric ions in the electroless copper plating solution into a salt of said alkaline earth metal, removing the precipitate from the plating solution, measuring at least one of the concentration of sulfuric ion in the plating solution (when the copper ion reducing agent is used) and the concentration of oxalic ion in the plating solution (when glyoxylic acid is used) and keeping an optimum sulfuric ion or oxalic ion concentration or preferentially 0.1 mol per liter or less of sulfuric ion and 0.2 mol per liter or less of oxalic ion during plating.

[3] An electroless copper plating machine using a plating solution containing copper sulfate as copper

ion sources, and copper ion complex, a copper ion
reducing agent or glyoxylic acid as a copper ion
reducing agent, and pH conditioner, wherein said
device comprises an electroless copper plating bath,
5 a reaction bath which adds at least one of alkaline
earth metal, alkaline earth metal hydroxide, alkaline
earth metal oxide, and alkaline earth metal salt
(excluding sulfuric salt) to said copper plating
solution therein to react with and precipitate
10 sulfuric ions or oxalic ion (when glyoxylic acid is
used) as an alkaline earth metal salt in said plating
solution, a filter unit which separates said metallic
salt precipitate, means for measuring at least one of
the concentration of sulfuric ion (when the copper ion
15 reducing agent is used) and the concentration of
oxalic ion in the plating solution (when glyoxylic
acid is used), and means for comparing at least one of
said measured concentrations by a preset reference
concentration and controlling the quantity of said
20 alkaline earth metal, alkaline earth metal hydroxide,
alkaline earth metal oxide, or alkaline earth metal
salt (excluding sulfuric salt) to be added.

[4] An electroless copper plating machine
using a plating solution containing metallic ions, an
25 agent for reducing said metallic ions, and a pH

conditioner, wherein said machine comprises An
electroless copper plating bath, a reaction bath
adding at least a metal or a compound containing a
metal to said plating solution to precipitate ions
5 which suppress generation of said plating metal, and a
ultrafiltration unit.

[5] Said filtration unit is preferably a cross-
flow type ultrafiltration unit or a filter press type
ultrafiltration unit.

10 [6] A multi-layer wiring board having insulating
layers and circuit layers accumulated and cemented
alternately wherein the circuit layers are
electrically connected by copper-plated through-holes
which pass through the insulating layer between said
15 circuit layers or by copper-plated via-holes whose one
end is closed and wherein the copper plating of said
multi-layer wiring board is made by said electroless
copper plating method.

[7] A module having one or more semiconductor
20 elements on said multi-layer wiring board.

The method of the present invention removes said
insoluble salt by saturating it at a temperature lower
than the plating temperature to cause it to
precipitate and ^{then} removing the precipitate. A method of
25 concentrating the plating solution can also be used to

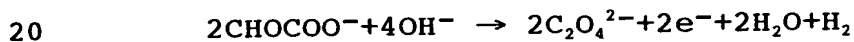
cause the insoluble salt to precipitate.

Removal of said insoluble salt can be done by circulating the plating solution while plating is in progress or in a batch manner when plating is not in progress after sulfuric ions and oxidant ions of the copper ion reducing agent in the non-electro plating solution exceed the preset quantities.

Below will be briefly explained a copper plating using copper sulfate as copper ion sources, as a copper ion source and glyoxylic acid as the copper ion reducing agent.

When copper sulfate, as copper ion sources, is used as a copper ion source, the sulfuric ions increase in the plating solution. When glyoxylic acid is used as a copper ion reducing agent, the glyoxylic acid behaves as glyoxalate ions in the plating solution and is reacted into oxalic ions which are [the] oxidant ions. This reaction is

(Reaction formula 1)



When the concentration of the byproduct ions exceeds a limit (0.1 mol per liter of sulfuric ions or 0.2 mol per liter of oxalic ions), the plating solution will lose its characteristics quickly.

Experimentally, the concentration of the byproduct

ions exceeds the limit when a plating layer of 30 to 60 μm thick is formed under conditions of a plating bath load of 1 dm^2 per liter.

When calcium hydroxide is added as a pH
5 conditioner, the sulfuric ions in the plating solution are precipitated as calcium sulfate and the concentration of remaining sulfuric ions will become very low (about 0.01 mol per liter or less) ^{same} (as) the solubility of calcium sulfate is about 0.15 gram
10 solute per 100 grams water at 60°C.

Similarly, the oxalic ions in the plating solution are precipitated as calcium oxalate and the concentration of remaining oxalic ions will become extremely low (about 7×10^{-6} mol per liter or less) ^{same} (as) the solubility of calcium oxalate is about 0.001 gram
15 solute per 100 grams water at 60°C. When the plating solution contains sulfuric ions of 0.01 mol per liter or less and the oxalic ions of 7×10^{-6} mol per liter or less, the plating characteristic is excellent and
20 the plated layer is very ductile.

Under this condition, no abnormal copper deposition is found on non-plating locations and the plating solution is also very stable. To add calcium ions into the plating solution, use a calcium pH
25 conditioner, calcium powder, calcium acetate, calcium

carbonate, calcium chloride, calcium oxide, and the like.

5 ^A
 (The) similar result can be obtained when calcium is
 ^{replaced}
 [substituted] by barium. When one of the above barium
compounds is used, almost all sulfuric ions in the
plating solution are precipitated as barium sulfate
and the concentration of remaining sulfuric ions will
become very low (about 1.5×10^{-4} mol per liter or
less) (as) ^{since} the solubility of barium sulfate is about
10 0.0036 gram solute per 100 grams water at 50°C.

 Similarly, the oxalic ions in the plating solution
are precipitated as barium oxalate and the
concentration of remaining oxalic ions will become
extremely low (about 7.9×10^{-5} mol per liter or less)
15 ^{since}
 (as) the solubility of barium oxalate is about 0.00175
gram solute per 100 grams water at 60°C.

 Air must be blown into the plating solution while
said compounds are added into the plating solution to
remove the precipitate of sulfuric and oxalic ions.
20 For addition of a substance which shows alkalinity in
an aqueous solution and increases the pH value of the
plating solution such as calcium hydroxide, barium
hydroxide, calcium powder, barium powder, and the like,
blowing air into the solution is always required while
25 the substance is added to the plating solution.

A plating method and a plating machine in accordance with the present invention do not limit ^{the choice of} a complexing agent for the electroless copper plating solution (hereinafter abbreviated as a copper plating solution). In other words, it can be any as far as it can form a stable complex with copper ions such as ethylenediaminetetraacetic acid (EDTA),

Rochelle salt, nitrilotriacetic acid (NTA),

nitrilotripropionic acid (NTP),

10 ethylenediaminediacetic acid (EDDA),

ethylenediaminepropionidihydrochloride (EDDP),

iminodiacetic acid (IDA),

trans-1.2-diaminocyclohexane-N,N,N'-tetraacetic acid (CyDTA),

15 diaminopropanoltetraacetic acid (DPTA-OH),

ethylenediaminediacetic acid (EDDA),

triethylenetetraaminehexaacetic acid (TTHA),

diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA),

20 dihydroxyethyl glycine (DHEG),

hydroxyethylenediaminetriacetic acid (EDTA-OH),

glycoletherdiaminetetraacetic acid (GEDTA),

nitrilotripropionic acid (NTP),

diaminopropanetetraacetic acid (Methyl-EDTA)

25 hydroxyethyliminodiacetic acid (HIDA),

ethylenediaminetetraquis (methylenesulfonic acid) (EDTPO), etc. As stated above, the sulfuric ions and the oxalic ions are precipitated and separated as insoluble salts from the plating solution and consequently the plating solution can ^{maintain} (keep the) optimum plating characteristics for a long time. The [flow] ^{Diagram} [sheet] of a machine which can offer such effects is illustrated in FIG. 1.

The plating bath 1 performs electroless copper plating (hereinafter abbreviated as copper plating). The copper plating solution is circulated along a circulation route 2 which passes through a filter column 3 (for separating floating objects such as dust or solid barium sulfate, barium oxalate, etc.). Part of the copper plating solution is sent to a reaction bath 4 and receives copper ions, ^a copper ion reducing agent, ^a and ^a pH conditioner, which are lost in plating there to recover the optimum concentrations. FIG. 1 shows a heat ^{exchanger} (exchange) 13 for heating the plating solution, a copper sulfate as copper ion sources, ^a supply tank 21, a pH conditioner supply tank ²² [2], a copper ion reducing agent supply tank 23, and circulation pumps 24, 25, and 27.

In the reaction bath, the concentrations of copper ions, copper ion reducing agent, and pH conditioner to

be added are necessarily higher than the concentrations of those in the plating bath, ^{so as} to recover the optimum concentrations of the plating solution in the plating bath with the fed-back copper plating solution. If calcium hydroxide or barium hydroxide is used as a pH conditioner, sulfuric ions and oxalic ions to be removed are precipitated as insoluble salts first in the reaction bath. Further, it sometimes happens that the concentrations of ingredients of the solution in the reaction bath are high enough to make the solution unstable.

In such a case, to prevent the copper plating solution from decomposing, a gas containing oxygen, such as ~~(the)~~ air, must be blown into the reaction bath through the gas supply pipe 5. If the solubilities of sulfuric salts and oxalic salts go lower as the liquid temperature falls, it is recommended to cool the copper plating solution in the reaction bath to increase the efficiency of precipitation.

In this case, the copper plating solution passing through a pre-cooling heat exchange 6 can be supplied to the reaction bath or the reaction bath itself can be cooled. ^{Since} (As), it is desirable to heat the cooled copper plating solution to a desired solution temperature before feeding it back to the plating bath,

the copper plating solution coming from the reaction bath is fed back to the plating bath through a heating heat ^{exchange} [exchange] 7.

5 A concentration analyzer 8 measures the concentration of copper ions, the concentration of the reducing agent, and the pH of the plating solution in the reaction tank. The quantities of ingredients to be supplied are controlled by pumps 9, 10, and 11 so that the measured concentrations may be [the] predetermined
10 concentrations. The concentrations of sulfuric ions and oxalic ions can be measured by chromatography. Part of the plating solution is taken out from the reaction bath for measurement. Besides chromatography, the measurement can be done by a capillary
15 electrophoresis analyzer.

The copper plating solution supplied with copper ions, copper ion reducing agent, and pH conditioner from the reaction bath is fed to a ultra filtration unit 12. The ultra filtration unit 12 contains an
20 ultra filtration membrane which separates the inner copper plating solution coming from the reaction bath from the outer copper plating solution coming from the plating bath. This is a cross-flow type ultra filtration unit. FIG.2 is a diagrammatic illustration
25 of the ultra filtration unit, ^{illustrating} [explaining] the principle

thereof. FIG.2 shows fine particles^d crystals 29, a cross-flow type ultra filtration unit 12, an ultra filtration membrane 31, a flow of plating solution 32, and a filtrate 33.

5 Using the characteristics of the ultra filtration unit that lets ions and low molecular organic compounds penetrate the membrane, but blocks fine particles, the solid precipitate produced in the reaction bath ^{is} (are) separated and removed out from the
10 system. In other words, only ions passing through the ultra filtration membrane can be fed back to the plating bath and solid components can be continuously removed from the system.

 In the cross-flow filtration, the copper plating
15 solution flows along the surface of the membrane. This prevents the membrane from being blocked quickly. Only the filtrate which passes through the membrane is fed back to the plating bath. This prevents the crystallized fine particles from returning to the
20 plating solution. The pore size of the membrane is 0.5 microns or less, preferentially 0.1 microns or less.

 The filtration ^{provided in accordance with} (of) the present invention can be any
^{type, so long} (as far) as sulfuric and oxalic salts produced in the
 reaction bath are not fed back to the plating bath.

25 Preferable filtration methods are a filter pressing

method, a cross-flow method, etc.

This method enables a long stable electroless copper plating (hereinafter abbreviated as copper plating) with sulfuric and oxalic ion concentrations low in the copper plating solution.

The purpose of the present invention can be realized with the use of a similar method and device [in accordance with the present invention] even when a compound which will not produce any insoluble salt, such as potassium hydroxide, etc., is used as a pH conditioner, when calcium or barium is added singly in the reaction bath or when calcium or barium carbonate, acetate, oxide, or chloride is added to the copper plating solution.

However, when calcium carbonate and/or barium carbonate are used, carbonic ions increase in the copper plating solution. When calcium acetate and/or barium acetate are used, acetic ions increase in the copper plating solution. Similarly, when calcium chloride and/or barium chloride are used, chloric ions increase in the copper plating solution.

Therefore, for the use of a calcium salt and/or a barium salt, the quantity of the salt should be such that its salt precipitate may not ^{exert} [give] any influence upon the plating characteristics. It is required to

estimate the influence of the salt in advance.

^{On the contrary}
[Contrarily], calcium hydroxide, barium hydroxide, calcium, barium, calcium oxide, and barium oxide (when added to the copper plating solution) will not increase ions in the copper plating solution and are preferable ^{since} (as) they can make the plating characteristics stable for a long time period.

Potassium hydroxide can be used as a pH conditioner even when calcium hydroxide and/or barium hydroxide are used to produce oxalic or sulfuric salt precipitate. Also, in this case, the purpose of the present invention can be realized.

In the above explanation, if the solubility of a compound (e.g. calcium hydroxide) to be added is low, a slurry of the compound is sometimes preferable to an aqueous solution of the compound. In this case, a slurry pump is usually used to feed the slurry compound to the reaction bath.

According to the present invention, byproduct ions, which increase as a non-electro plating reaction advances, can be eliminated, and, consequentially, the electroless copper plating solution can have a longer working life, drastically reducing the plating cost.

BRIEF DESCRIPTION OF DRAWINGS

FIG.1 is a [flow] diagram, ^{illustrating} [explaining] the configuration of a plating machine in accordance with the present invention.

5 FIG.2 is a schematic diagram of the ultra filtration unit used in the plating machine in accordance with the present invention.

FIG.3 is a [flow] diagram ^{illustrating} [explaining] the configuration of a plating machine ^{according to} [which is] a preferred embodiment of the present invention.

10 FIG.4 is a [flow] diagram, ^{illustrating} [explaining] the configuration of a plating machine ^{according to} [which is] another preferred embodiment of the present invention.

FIG.5 is a [flow] diagram, ^{illustrating} [explaining] the configuration of a plating machine ^{according to} [which is] another preferred embodiment of the present invention.

15 FIG.6 is a schematic sectional diagram of a module having semiconductor elements on a multi-layer board plated in accordance with the present invention.

20

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[Embodiment 1]

A first embodiment of the present invention uses
25 copper sulfate as copper ion sources, as a copper ion

source, glyoxylic acid as a copper ion reducing agent and barium hydroxide as a pH conditioner. This embodiment uses EDTA pentasodium as a complexing agent because the solubility of barium hydroxide is not so great.

Below are listed the ingredients of the plating solution and the plating condition.

(Ingredients)

- Copper (II) sulfate pentahydrate 0.04 mol per liter
- EDTA pentasodium 0.1 mol per liter
- Glyoxylic acid 0.03 mol per liter
- Barium hydroxide 0.01 mol per liter
- 2,2' bipyridyl 0.0002 mol per liter
- Polyethylene glycol (mean molecular weight = 600) 0.03 mol per liter

The concentration of barium hydroxide is controlled to keep the pH of the plating solution at 12.3.

(Plating condition)

- pH 12.3
- plating solution temperature 70°C

A copper wiring pattern was plated on a test board in said copper plating solution. The stability of the plating solution and the quality of the plated layer

were evaluated from the existence of ^{an} abnormal deposition of copper. The test board was prepared as stated below. The physical property of the plated layer was also evaluated.

5 (Preparation of a test board)

A test board was prepared by coating both surfaces of a 0.6mm-thick glass-sheet reinforced resin laminated board with an adhesive containing acrylonitrilebutadiene rubber modified phenol resin as the main ingredient, and hardening ^{the test board} ~~thereof~~ at 160°C for
10 ten minutes. The hardened test board has an adhesive layer of about 30 microns thick on each surface. Then, the test board was drilled at preset locations and dipped in a coarsening liquid containing chromic
15 anhydride and hydrochloric acid to coarsen the adhesive surfaces.

Next, the board was dipped for ten minutes in a single-liquid palladium colloidal catalyst solution (fabricated by Hitachi Kasei Co., Ltd. acid aqueous
20 solution containing intensifier HS101B) as a copper plating catalyst, washed clean with water, and dried up at 120°C for 20 minutes.

Both surfaces of the board were coated with a dry-film photo-resist layer ~~[of]~~ 35 microns thick (SR-3000
25 fabricated by Hitachi Kasei Co., Ltd). A mask of a

test pattern comprising lines of 60 microns thick was placed on the photo resist surface of the board. The board was exposed to light and developed. As (the)^A result, the non-pattern parts on the surface of the board are all covered with the photo-resist.

The test board prepared above and a stainless steel plate were both dipped in the plating solution at a liquid temperature of 70°C and plated with a load of 1 dm² per liter.

The stainless steel plate was prepared by dipping the plate in 17% hydrochloric aqueous solution for 2 minutes, dipping it in the above palladium collidal solution for 10 minutes, and washing it thoroughly. While plating is in progress, air was blown into the plating solution to stir up the solution. A prepared liquid (listed below) was supplied to the plating solution to make the concentration of copper ions, the concentration of glyoxylic acid (copper ion reducing agent), and the pH constant.

(1) Copper ion supplement ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 200 grams
Water Quantity required to make one liter of the solution

(2) Glyoxylic acid (copper ion reducing agent)
supplement 40% glyoxylic acid solution

(3) pH conditioner ($\text{Ba}(\text{OH})_2$) 40 grams

Water Quantity required to make one liter of the solution

One plating cycle comprises a plating step to form a 30 μ m-thick copper layer on the stainless steel plate and the pattern area of the test board. At the end of each plating cycle, the plated copper layer was peeled off from the stainless steel plate, cut into a piece of 1.25 cm by 10 cm. The mechanical strength of the piece was measured by an ordinary tensile tester.

The precipitates (barium sulfate, barium oxalate, and others) which were formed during plating were filtered and removed by circulation and filtration of the plating solution. After each plating cycle is completed, the plating solution is cooled down to [the] room temperature (25°C) and filtered to remove the precipitates (barium sulfate, barium oxalate, and others) before the succeeding plating cycle. The concentrations of the sulfuric and oxalic ions in this clean plating solution were measured by chromatography. Table 1 shows the result of the measurement.

Table 1

		Unit	Number of plating cycles						
			1	2	3	4	5	6	7
5	Embodiment 1	Conc. of sulfuric ions	mol/l	8×10^{-3}	9×10^{-3}	9×10^{-3}	8×10^{-3}	8×10^{-3}	8×10^{-3}
		Conc. of oxalic ions	mol/l	7×10^{-6}	7×10^{-6}	7×10^{-6}	6×10^{-6}	7×10^{-6}	6×10^{-6}
		Ductility of plate film	%	9.8	10.5	9.7	10.1	7.8	10.3
		Abnormal deposition	-	None	None	None	None	None	None
10	Embodiment 2	Conc. of sulfuric ions	mol/l	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}
		Conc. of oxalic ions	mol/l	7×10^{-5}	7×10^{-5}	6×10^{-5}	7×10^{-5}	6×10^{-5}	5×10^{-5}
		Ductility of plate film	%	10.1	8.5	9.6	7.1	6.8	10.2
		Abnormal deposition	-	None	None	None	None	None	None
15	Embodiment 3	Conc. of sulfuric ions	mol/l	9×10^{-3}	9×10^{-3}	8×10^{-3}	8×10^{-3}	9×10^{-3}	8×10^{-3}
		Conc. of formic ions	mol/l	0.12	0.28	0.42	0.62	0.78	1.12
		Ductility of plate film	%	10.5	8.8	7.5	6.8	5.2	4.6
		Abnormal deposition	-	None	None	None	None	Little	Little
20	Embodiment 4	Conc. of sulfuric ions	mol/l	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}
		Conc. of formic ions	mol/l	0.11	0.26	0.43	0.62	0.77	1.18
		Ductility of plate film	%	11.0	10.2	7.6	7.3	5.5	4.3
		Abnormal deposition	-	None	None	None	None	Little	Little
25	Embodiment 6	Conc. of sulfuric ions	mol/l	9×10^{-3}	9×10^{-3}	9×10^{-3}	8×10^{-3}	8×10^{-3}	8×10^{-3}
		Conc. of oxalic ions	mol/l	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-6}
		Ductility of plate film	%	10.2	8.7	9.6	8.8	8.5	9.8
		Abnormal deposition	-	None	None	None	None	None	None
	Comparative embodiment 1	Conc. of sulfuric ions	mol/l	0.08	0.12	0.19	0.35	0.55	-
		Conc. of formic ions	mol/l	0.12	0.24	0.38	0.67	0.98	-
		Ductility of plate film	%	9.8	7.5	5.4	3.2	1.2	-
		Abnormal deposition	-	None	Little	Some	Some	Deposition	-
	Comparative embodiment 2	Conc. of sulfuric ions	mol/l	0.08	0.13	0.18	0.33	0.56	-
		Conc. of oxalic ions	mol/l	0.12	0.24	0.37	0.77	1.02	-
		Ductility of plate film	%	9.7	7.7	5.2	2.8	1.0	-
		Abnormal deposition	-	None	Little	Some	Some	Deposition	-

The concentrations of sulfuric and oxalic ions in the plating solution were measured after the plating solution was filtered at the end of each plating cycle.

5 Even after seven plating cycles, the sulfuric ion concentration was 1.5×10^{-4} mol per liter or less and the oxalic ion concentration was 7.9×10^{-5} mol per liter or less. The ductility of the obtained plated layer was 6% or more and was not deteriorated so much
10 as the number of plating cycles increased. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady even after seven plating cycles were ^{completed} ~~made~~.

15 As stated above, the method in accordance with the present invention ^{was} ~~(is)~~ found to suppress ^{any} increase of sulfuric and oxalic ions in the plating solution. This is due to the use of barium hydroxide as a pH conditioner which causes the sulfuric and oxalic ions
20 to precipitate as insoluble barium salts. This precipitate is separated from the plating solution, and ^{so} the plating solution can be almost free from sulfuric and oxalic ions.

The long excellent plating characteristics can be
25 obtained by plating under conditions of the sulfuric

ion concentration of 0.1 mol per liter or less and the oxalic ion concentration of 0.2 mol per liter or less in the plating solution.

[Embodiment 2]

5 A second embodiment of the present invention was
 ^{carried out}
 (done) under the same conditions as the first embodiment,
 but barium hydroxide as a pH conditioner was
 substituted by calcium hydroxide. As the solubility of
 calcium hydroxide is very low (approx. 1.7 gram solute
10 per 1 liter water), its aqueous solution is not
 available. Therefore calcium hydroxide in slurry
 (obtained by powering calcium hydroxide and adding
 pure water thereto) was used.

 Powdered calcium hydroxide has greater surfaces in
15 contact with the plating solution and can easily react
 with sulfuric and oxalic ions into insoluble
 precipitates in the plating solution, although the
 solubility of calcium hydroxide is very low. In this
 case, however, the efficiency of removal of sulfuric
20 and oxalic ions from the plating solution is dependent
 upon the granule sizes of the calcium hydroxide powder,
 the rate of solution stirring, and so on. They must be
 optimized in advance.

 To prevent a lot of crystals including un-
25 dissolved calcium hydroxide from existing in the

plating solution, this embodiment employs a method of adding a slurry of calcium hydroxide into the reaction bath, which is provided separately from the plating bath, instead of adding a slurry of calcium hydroxide directly into the plating bath, mixing the slurry and the plating solution in the plating bath, removing the precipitate by the ultra filtration unit, and feeding back the filtered plating solution to the plating bath.

Table 1 shows the result of ^{an} evaluation of ^{the} plating characteristics. This method can keep the sulfuric and oxalic concentrations very low (0.01 mol per liter or less of sulfuric ion and 7×10^{-6} mol per liter or less of oxalic ion) even after seven plating cycles.

The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after many plating cycles. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady even after seven plating cycles were ^{completed} made.

[Embodiment 3]

A third embodiment of the present invention uses copper sulfate as copper ion sources, as a copper ion source, formaldehyde as a copper ion reducing agent and barium hydroxide as a pH conditioner. In this case,

the oxidant ion of the formaldehyde is formic acid. This embodiment assumes that formic acid cannot be removed as a precipitate. Below are listed the ingredients of the plating solution and the plating
5 condition.

(Ingredients)

- Copper (II) sulfate pentahydrate 0.04 mol per
liter

- EDTA pentasodium 0.1 mol per liter

10 - Formaldehyde 0.03 mol per liter

- Barium hydroxide 0.01 mol per liter

- 2,2' bipyridyl 0.0002 mol per liter

- Polyethylene glycol

(mean molecular weight = 600) 0.03 mol per liter

15 The concentration of barium hydroxide is
controlled to keep the pH of the plating solution at
12.3.

(Plating condition)

- pH 12.3

20 - Liquid temperature 70°C

This embodiment plated the same test board ^{using} (in) the
same method as Embodiment 1 in the above copper
plating solution. The physical property of the
obtained plated layer (foil), abnormal deposition, and
25 concentrations of salts in the plating solution were

tested and measured in the same manner as Embodiment 1. 37% formaldehyde aqueous solution is used to supply the copper ion reducing agent.

Table 1 shows the result of ^{an}evaluation of ^{the}plating characteristics. The concentration of sulfuric ions in the plating solution was measured after the plating solution was filtered at the end of each plating cycle.

This method can keep the sulfuric concentration very low (1.5×10^{-4} mol per liter or less) even after seven plating cycles.

The ductility of the plated layer (foil) formed in the seventh plating cycle was under half as much as that of the plated layer (foil) formed in the first plating cycle, but it was strong enough to assure the reliability. Further, within five plating cycles, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady. After ^{the}sixth and seventh plating cycles, a little abnormal deposition was found on the test board and in the plating bath, but it was not ^{significant}(much) enough to cause short-circuiting of a wiring pattern on the test board.

[Embodiment 4]

A fourth embodiment of the present invention was ^{carried out}(done) under the same conditions as the third embodiment,

but the pH conditioner for the plating solution and
the supplement ^{was} [is] calcium hydroxide. As the solubility
of calcium hydroxide is very low, its aqueous solution
is not available. Therefore calcium hydroxide (in
5 slurry) was used as in the second embodiment.

The result of measurement is listed in Table 1.
This method can keep the sulfuric concentration very
low (0.01 mol per liter or less) after the seven
plating cycles. The ductility of the plated layer
10 (foil) formed in the seventh plating cycle was under
half as much as that of the plated layer (foil) formed
in the first plating cycle, but it was strong enough
to assure ^{required} the reliability.

Further, within five plating cycles, no abnormal
15 deposition was visually detected on the test board, in
the plating bath, pipings, and so on. The plating
solution was extremely steady. After ^{the} sixth and seventh
plating cycles, a little abnormal deposition was found
on the test board and in the plating bath, but it was
20 not ^{significant} [much] enough to cause short-circuiting of a wiring
pattern on the test board.

[Embodiment 5]

A copper plating solution of a fifth embodiment of
the present invention was prepared using copper
25 sulfate as copper ion sources, as a copper ion source,

glyoxylic acid as a copper ion reducing agent and potassium hydroxide as a pH conditioner in preparation of a plating solution.

(Ingredients)

- | | | |
|----|------------------------------------|--|
| 5 | - Copper (II) sulfate pentahydrate | 0.04 mol per liter |
| | - EDTA pentasodium | 0.1 mol per liter |
| | - Glyoxylic acid | 0.03 mol per liter |
| | - Potassium hydroxide | 0.03 mol per liter |
| 10 | - 2,2' bipyridyl | 0.0002 mol per liter |
| | - Polyethylene glycol | (mean molecular weight = 600) 0.03 mol per liter |

The concentration of potassium hydroxide is controlled to keep the pH of the plating solution at 12.3.

(Plating condition)

- | | |
|----------------------|------|
| - pH | 12.3 |
| - Liquid temperature | 70°C |

A prepared liquid (listed below) was supplied to the plating solution to make the concentration of copper ions, the concentration of glyoxylic acid (a copper ion reducing agent), and the pH constant, although they decrease as ^{the} (a) plating advances.

- (1) Copper ion supplement ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 200 grams
- 25 Water Quantity required to make one liter of

the solution

(2) Glyoxylic acid (copper ion reducing agent)
supplement 40% glyoxylic acid solution

(3) pH conditioner ($\text{Ba}(\text{OH})_2$) 40 grams

5 Water Quantity required to make one liter of
the solution

As seen from the above, ^{an} aqueous solution of barium
hydroxide is used to keep the pH of the plating
solution constant, although potassium hydroxide is used
10 as a pH conditioner when the plating solution is
prepared.

Even after seven plating cycles, the sulfuric ion
concentration was 1.5×10^{-4} mol per liter or less and
the oxalic ion concentration was 7.9×10^{-5} mol per
15 liter or less. The ductility of the obtained plated
layer was 6% or more and was not deteriorated so much
as the number of plating cycles increased. Further, no
abnormal deposition was visually detected on the test
board, in the plating bath, pipings, and so on. The
20 plating solution was extremely steady even after seven
plating cycles were ^{completed} made.

[Embodiment 6]

A sixth embodiment of the present invention uses a
plating solution containing copper sulfate as copper
25 ion sources, as a copper ion source, glyoxylic acid

reaction bath 4 and receives copper ions,^a copper ion
reducing agent, and^a pH conditioner to supplement the
lost quantities of ingredients. The composition of the
supplemental solution is listed below.

- 5 (1) Copper ion supplement ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 200
grams

Water Quantity required to make one liter of
the solution

- (2) Glyoxylic acid (copper ion reducing agent)
10 supplement 40% glyoxylic acid solution

- (3) pH conditioner (KOH) 200 grams

Water Quantity required to make one liter of
the solution

Calcium powder was added to the plating solution
15 in the reaction bath to react with sulfuric and oxalic
ions into insoluble salts. As the pH of the plating
solution increases when the calcium powder is added,
the pH conditioner is added to the plating solution to
decrease the pH. Further, the calcium powder generates^a
20 heat of dissolution when it dissolves into the plating
solution. [You must take a very^{thus,} care^{must be taken} when dissolving
the powder.

Therefore, the reaction bath was cooled for
efficient separation of the precipitate of oxalic salt.

25 When the calcium powder is added, the plating

solution has lots of precipitates (calcium sulfate, calcium oxalate, and calcium particles which remain un-dissolved). Embodiment 6 removed these precipitates from the plating solution by ^{means of} the ultra filtration unit, regulated the concentration of copper ions, the concentration of glyoxylic acid and the pH to predetermined values, ^{and} then fed back the plating solution to the plating bath 1.

Table 1 shows the result of ^{an} evaluation of ^{the} plating characteristics (the concentration of sulfuric ions, the concentration of oxalic ions, the ductility of the plated layer, and detection of abnormal deposition) of each plating cycle.

The concentration of sulfuric ions and the concentration of oxalic ions in the table are the result of measurement after each plating cycle is completed. This embodiment can keep the sulfuric and oxalic concentrations very low (0.01 mol per liter or less of sulfuric ion and 7×10^{-6} mol per liter or less of oxalic ion) even after seven plating cycles.

The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after many plating cycles. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating

solution was extremely steady even after seven plating cycles were ^{completed} ~~made~~.

[Embodiment 7]

5 A seventh embodiment of the present invention was ^{carried out} ~~done~~ under the same conditions as Embodiment 6, but calcium powder ^{was replaced} ~~is substituted~~ by barium oxide to react with sulfuric and oxalic ions into precipitates. The testing method of this embodiment is the same as Embodiment 6.

10 This embodiment can keep the sulfuric and oxalic concentrations very low (1.5×10^{-4} mol per liter or less of sulfuric ion and 7.9×10^{-5} mol per liter or less of oxalic ion) even after seven plating cycles. The ductility of the obtained copper layer (foil) was
15 6% or more and remained almost unchanged even after many plating cycles. Further, no abnormal deposition was visually detected on the test board, in the plating bath, pipings, and so on. The plating solution was extremely steady even after seven plating cycles
20 were ^{completed} ~~made~~.

[Embodiment 8]

An eighth embodiment of the present invention was ^{carried out} ~~done~~ under the same conditions as Embodiment 6, but calcium powder ^{was replaced} ~~is substituted~~ by barium carbonate to
25 react with sulfuric and oxalic ions into precipitates.

The testing method of this embodiment is the same as Embodiment 6.

This embodiment can keep the sulfuric and oxalic concentrations very low (1.5×10^{-4} mol per liter or less of sulfuric ion and 7.9×10^{-5} mol per liter or less of oxalic ion) even after seven plating cycles. The ductility of the obtained copper layer (foil) was 6% or more and remained almost unchanged even after many plating cycles.

10 However, it was found, ^{that} the plating rate ^{was} reduced as the carbonate increased in the plating solution. As ^a the result of visual checks, the plating solution was extremely steady even after seven plating cycles were ^{completed} made, but a little abnormal deposition was found on
15 the test board.

As stated above, the most excellent barium compound to be added to the plating solution to react with sulfuric and oxalic ions into precipitates is barium oxide, barium hydroxide, or ^a simple substance of barium ^{as well} (as) they will not increase ions in the plating
20 solution.

Although barium carbonate added to the plating solution as in this embodiment can suppress ^{an} increase of sulfuric and oxalic ions in the plating solution, ^{an}
25 increase of carbonate ions was recognized. However,

the plating characteristic of this embodiment is better than that of a method which does not use this embodiment. By plating with ^athe concentration of sulfuric ions ^a0.1 mol per liter and ^athe concentration of oxalic ions ^a0.2 mol per liter in the plating solution, ^athe excellent plating characteristic can be ^{maintained}kept for a long time. This is the effect of this embodiment.

[Embodiment 9]

10 A ninth embodiment of the present invention was ^{carried out}done under the same conditions as Embodiment 6, but calcium powder ^{was replaced}is substituted by barium acetate to react with sulfuric and oxalic ions into precipitates. The testing method of this embodiment is the same as
15 Embodiment 6.

This embodiment can keep the sulfuric and oxalic concentrations very low (1.5×10^{-4} mol per liter or less of sulfuric ion and 7.9×10^{-5} mol per liter or less of oxalic ion) even after seven plating cycles.
20 The ductility of the obtained copper layer (foil) was 3% or more and a little inferior to that of the embodiment using barium hydroxide. As ^athe result of visual checks, the plating solution was extremely steady even after seven plating cycles were ^{completed}made, but
25 a little abnormal deposition was found on the test

board. It is assumed that this is caused by the increase of acetic ions in the plating solution assumed.

Although barium acetate added to the plating solution as in this embodiment can suppress^{an} increase of sulfuric and oxalic ions in the plating solution,^{an} increase of acetate ions was recognized. However, the plating characteristic of this embodiment is better than that of a method which does not use this embodiment. By plating with ^a(the) concentration of sulfuric ions^d 0.1 mol per liter and ^a(the) concentration of oxalic ions^d 0.2 mol per liter in the plating solution, ^{an}(the) excellent plating characteristic can be ^{maintained} kept for a long time.

15 [Embodiment 10]

A tenth embodiment of the present invention was ^{carried out} done under the same conditions as Embodiment 6, but calcium powder ^{was replaced} (is substituted) by barium chloride to react with sulfuric and oxalic ions into precipitates. 20 The testing method of this embodiment is the same as Embodiment 6.

This embodiment can keep the sulfuric and oxalic concentrations very low (1.5×10^{-4} mol per liter or less of sulfuric ion and 7.9×10^{-5} mol per liter or less of oxalic ion) even after seven plating cycles. 25

The ductility of the obtained copper layer (foil) was 3% or more and a little inferior to that of the embodiment using barium hydroxide. As ⁹the result of visual checks, the plating solution was extremely steady even after seven plating cycles were ^{completed} made, but a little abnormal deposition was found on the test board. It is assumed that this is caused by the increase of chloric ions in the plating solution [assumed] _^.

10 As stated above, the most excellent barium compound to be added to the plating solution to react with sulfuric and oxalic ions into precipitates is barium hydroxide, barium oxide, or ^asimple substance of barium ^{since} (as) they will not increase ions in the plating solution.

15 Although barium chloride added to the plating solution as in this embodiment can suppress ^{an} increase of sulfuric and oxalic ions in the plating solution, ^{an} increase of chloride ions was recognized. However, the plating characteristic of this embodiment is better than that of a method which does not use this embodiment. By plating with ⁹the concentration of sulfuric ions ^d0.1 mol per liter and ⁹the concentration of oxalic ions ^d0.2 mol per liter in the plating solution, ^{an}the excellent plating characteristic can be

maintained
1 [kept] for a long time. This is the effect of this
embodiment.

[Embodiment 11]

This embodiment of the present invention was *carried out* [done],
5 under the same conditions as Embodiment 6, but calcium, *was replaced*
to be added to the plating solution [is substituted] by
barium to react with sulfuric and oxalic ions into
precipitates.

This embodiment can keep the sulfuric and oxalic
10 concentrations very low (1.5×10^{-4} mol per liter or
less of sulfuric ion and 7.9×10^{-5} mol per liter or
less of oxalic ion) even after seven plating cycles.
The ductility of the obtained copper layer (foil) was
6% or more and remained almost unchanged even after
15 many plating cycles. Further, no abnormal deposition
was visually detected on the test board, in the
plating bath, pipings, and so on. The plating solution
was extremely steady even after seven plating cycles
were *completed* [made].

20 [Embodiment 12]

A twelfth embodiment of the present invention uses
copper sulfate as copper ion sources, as a copper ion
source, formaldehyde as a copper ion reducing agent
and potassium hydroxide as a pH conditioner. In this
25 case, the oxidant ion of the formaldehyde is formic

acid. This embodiment assumes that formic acid cannot be removed as a precipitate. Below are listed the ingredients of the plating solution and the plating condition.

5 (Ingredients)

- Copper (II) sulfate pentahydrate
0.04 mol per liter
- EDTA pentasodium 0.1 mol per liter
- Formaldehyde 0.03 mol per liter
- 10 - Potassium hydroxide 0.03 mol per liter
- 2,2' bipyridyl 0.0002 mol per liter
- Polyethylene glycol
(mean molecular weight = 600) 0.03 mol per liter

The concentration of potassium hydroxide is
15 controlled to keep the pH of the plating solution at 12.3.

(Plating condition)

- pH 12.3
- Liquid temperature 70°C

20 This embodiment plated the same test board ^{using} (in) the same method as Embodiment 1 in the above copper plating solution ^{in the} (in) plating flow illustrated in FIG.1.

The copper plating solution is circulated along a circulation route 2 which passes through a filter
25 column 3.

Part of the copper plating solution is sent to a reaction bath 4 and receives copper ions,^a copper ion reducing agent, and^a pH conditioner, which are lost in plating there, to recover the optimum concentrations.

5 The composition of the supplemental solution is listed below.

(1) Copper ion supplement ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 200 grams

10 Water Quantity required to make one liter of the solution

(2) Formaldehyde (copper ion reducing agent) supplement 37% glyoxylic acid solution

(3) pH conditioner (KOH) 200 grams

15 Water Quantity required to make one liter of the solution.

Calcium powder was added to the plating solution in the reaction bath to react with sulfuric ions into insoluble salt. As the pH of the plating solution increases when the calcium powder is added, the pH conditioner was added to the plating solution to decrease the pH. Further, the calcium powder generates a lot of heat of dissolution when it dissolves into the plating solution. [You must take a very^{thus,} care^{must be taken} when dissolving the powder. Therefore, the reaction bath was cooled for efficient separation of the precipitate

25

of oxalic salt.

When the calcium powder is added, the plating solution has lots of precipitates (calcium sulfate and calcium particles which remain un-dissolved). This
5 embodiment removed these precipitates from the plating solution ^{means of} by the ultra filtration unit, regulated the concentration of copper ions, the concentration of formaldehyde and the pH to predetermined values, ^{and} then fed back the plating solution to the plating bath 1.

10 This embodiment can keep the sulfuric concentration very low (1.5×10^{-4} mol per liter or less) even after seven plating cycles. The ductility of the plated layer (foil) formed in the seventh plating cycle was 3% which is under half as much as
15 that of the plated layer (foil) formed in the first plating cycle, but it was strong enough to assure the reliability.

Further, within five plating cycles, no abnormal deposition was visually detected on the test board, in
20 the plating bath, pipings, and so on. The plating solution was extremely steady. After ^{the} sixth and seventh plating cycles, a little abnormal deposition was found on the test board and in the plating bath, but it was not ^{significant} ~~(much)~~ enough to cause short-circuiting of a wiring
25 pattern on the test board.

[Comparative embodiment 1]

This embodiment performed copper plating using a conventional copper plating solution which contained formaldehyde as a copper ion reducing agent and sodium hydroxide as a pH conditioner.

The pH and the temperature of the plating solution were respectively 12.5 and 70°C. In this case, the oxidant ion of the formaldehyde is formic acid and the solubility of sodium formate is extremely high (99.6 grams solute per 100 grams water at 25°C). Further, the solubility of sodium sulfate is also high (21.9 grams solute per 100 grams water at 25°C). Therefore, sodium formate and sodium sulfate will never precipitate even after the copper plating solution is cooled, and these ions (byproduct ions) cannot be removed.

The concentration of sulfuric ions, the concentration of formic ions, and the physical quantity of the plated layer (foil) in repetitive plating are illustrated in Table 1.

Table 1 shows that, as the repetitive plating advances, the sulfuric and formic ions increase in the plating solution and the ductility of the plated layer (foil) decreases. Further, the copper plating solution became unstable as the plating advanced. The plating

solution started autolysis halfway in the fifth
plating and was ^{unable} [disabled] to plate.

[Comparative embodiment 2]

5 This embodiment performed copper plating using the
same copper plating solution as Comparative Embodiment
2 but calcium hydroxide as the pH conditioner was
[substituted] ^{replaced} by potassium hydroxide. The pH and the
temperature of the plating solution were respectively
12.5 and 70°C.

10 In this case, the solubility of potassium sulfate
is high (10.8 grams solute per 100 grams water at 25°C).
Therefore, sodium sulfate will never precipitate, and ^{so}
the sulfuric ions cannot be removed.

15 Similarly, the solubility of potassium oxalate is
also high (35.9 grams solute per 100 grams water at
25°C). Therefore, potassium oxalate did not
precipitate even after the copper plating solution was
cooled, and ^{so} the oxalic ions could not be removed.

20 The concentration of sulfuric ions, the
concentration of oxalic ions, and the physical
quantity of the plated layer (foil) in repetitive
plating are illustrated in Table 1.

25 Table 1 shows that, as the repetitive plating
advances, the ^{amount of} sulfuric and oxalic ions increases in
the plating solution and the ductility of the plated

layer (foil) decreases. Further, the copper plating solution became unstable as the plating advanced. The plating solution started autolysis halfway in the fifth plating and was ^{unable} ~~(disabled)~~ to plate.

5 As seen from the above, it is apparatus that use methods which are not in accordance with the present invention ~~that~~ cause blocking ions to increase in the plating solution ^{with} ~~(and)~~ the ^{result that the} ~~(resulting)~~ plating characteristics are deteriorated. This has proven that
10 the present invention has ^{an} ~~(the)~~ advantage.

[Embodiment 13]

Below will be explained a plating machine which is one ~~[of the]~~ embodiment in accordance with the present invention. FIG.3 is a ~~[flow]~~ diagram showing the
15 configuration of a plating machine in accordance with the present invention.

The copper plating was ^{carried out} ~~(made)~~ in the plating bath 1. The copper plating solution is circulated through a filtration column 3 along a circulation path 2 to
20 remove solids floating in the copper plating solution. The device has another circulation path passing through a heat ^{exchanger} ~~(exchange)~~ 13 to heat up the copper plating solution to a predetermined temperature.

Part of the copper plating solution is sent to a
25 reaction bath 4 and receives copper ions, ^a copper ion

reducing agent, and^a pH conditioner to supplement the lost quantities of ingredients.

In the reaction bath 4, the concentrations of copper ions, copper ion reducing agent, and pH conditioner to be added are necessarily higher than the concentrations of those in the plating bath to recover the optimum concentrations of the plating solution in the plating bath 1 with the fed-back copper plating solution.

To prevent the copper plating solution from decomposing in the reaction bath 4, a gas containing oxygen (gas), such as (the) air, is blown into the copper plating solution in the reaction bath through a gas supply valve 5 to stir up the solution with the gas. A concentration analyzer 8 measures the concentration of copper ions, the concentration of the reducing agent, and the pH of the plating solution in the reaction tank. The quantities of ingredients to be supplied are controlled by pumps 9, 10, and 11 so that the measured concentrations may be (the) predetermined concentrations.

Pumps 9, 10, and 11 respectively supply copper sulfate as copper ion sources, aqueous solution, glyoxylic acid aqueous solution, and barium hydroxide aqueous solution in that order.

The concentrations of copper ions, the copper ion

reducing agent, and the pH conditioner of the copper
plating solution in the reaction bath are higher than
those of the plating solution in the plating bath.
Barium sulfate and barium oxalate are saturated and
5 precipitated first in the reaction bath 4 as the
copper plating solution is cooled by the heat ^{exchanger} [exchange] 1
6 before entering the reaction bath 4.

These precipitates (fine crystallized particles)
are separated from the copper plating solution by the
10 cross-flow type ultra filtration unit 12. The filtered
clean copper plating solution is fed back to the
plating bath through the heating heat ^{exchanger} [exchange] 7.

The copper plating solution containing a lot of
precipitate is sent to the settling bath 14 in the
15 , upstream side of the reaction bath 4. Only the
supernatant plating solution overflows a weir which is
provided between the settling bath 14 and the reaction
bath 4 back into the reaction bath 4.

70% or more of the solid precipitate in the copper
20 plating solution sent to the settling bath 14 remains
settled and is taken out of the system.

As stated above, the device in accordance with the
present invention can remove sulfuric and oxalic ions
which deteriorate the plating characteristics as
25 barium salts and ^{maintain} (keep) an excellent plating

characteristic for a long time.

[Embodiment 14]

FIG.4 is a flow diagram of a plating machine using a filter press type ultra filtration unit. This
5 embodiment uses almost the same units as those of Embodiment 13 and performs [the] similar operations. [The] ^{an} explanation ^{thereof} is omitted here. Unit 17 is a recovery tank.

This embodiment is characterized in that the whole
10 reaction bath 4 is cooled further by water sent from the cooling unit 15 after part of the copper plating solution is supplied to the reaction bath 4.

The concentrations of copper ions, the copper ion
reducing agent, and the pH conditioner of the copper
15 plating solution in the reaction bath 4 are higher than those of the plating solution in the plating bath 1, and the reaction bath 4 is cooled by water from the cooling unit 15. Therefore, barium sulfate and barium oxalate are first saturated and easily precipitated in
20 the reaction bath.

These precipitates (fine crystallized particles) are separated from the copper plating solution by the filter press type ultra filtration unit 16. The filtered clean copper plating solution is fed back to
25 the plating bath 1 through the heating heat ^{exchanger} [exchange] 7.

The precipitate caught by the filter press type ultra filtration unit 16 is scaled off from the filter membrane into the recovery tank 17 through a funnel-shaped collecting means, and taken out from the system.

5 As stated above, the device in accordance with the present invention can remove sulfuric and oxalic ions which deteriorate the plating characteristics as barium salts and ^{maintain} (keep) an excellent plating characteristic for a long time.

10 [Embodiment 15]

This embodiment uses a copper plating solution containing barium hydroxide or calcium hydroxide as a pH conditioner. FIG.5 is a flow diagram of a plating machine using alkaline metal hydroxide such as sodium
15 hydroxide or potassium hydroxide as a pH conditioner. FIG.5 contains a delivery pump 26 and an alkali earth metal salt supply tank 28.

The reaction bath 4 is equipped with a supply pump 18 for supplying aqueous solution containing at least
20 one of calcium hydroxide, barium hydroxide, calcium carbonate, barium carbonate, calcium acetate, barium acetate, calcium oxide, barium oxide, calcium, and barium to react with sulfuric and oxalic ions into precipitates.

25 The quantities of chemicals to precipitate the

ions are regulated by a pump 9 for supplying copper sulfate as copper ion sources, aqueous solution, a pump 10 for supplying glyoxylic acid aqueous solution, and an analyzing unit 8.

5 The quantity of sulfuric ions in the copper plating solution can be calculated from the quantity of copper sulfate as copper ion sources, solution supplied by pump 9. The quantity of oxalic ions in the copper plating solution is calculated as the
10 difference between the quantity of oxalic acid solution measured by the analyzing unit 8 and the quantity of the existing glyoxylic acid. The copper plating solution control unit 19 performs these
15 calculations and controls the pump 18 according to the result of calculation. The other configuration of this embodiment is the same as that of Embodiment 13 and Embodiment 14.

As stated above, the device in accordance with the present invention can remove sulfuric and oxalic ions
20 which deteriorate the plating characteristics as barium salts and ^{maintain} ~~keep~~ an excellent plating characteristic for a long time.

[Embodiment 16]

FIG.6 is a ^{diagrammatic} ~~diagrammatical~~ sectional view of a
25 module comprising a multi-layer wiring board 54

produced by a copper plating method in accordance with the present invention and semiconductor elements thereon. A number 45 indicates an insulating layer.

5 The multi-layer wiring board 54 is prepared by forming a wiring pattern on each board with a known photo-resist, plating a conductor wiring 34 on the board by a method stated in said embodiments, and piling a preset number of said plated boards with an insulating layer 37 therebetween.

10 The conductor wirings on the plated boards are electrically connected by via-holes 36 and through-holes 35 which are drilled in advance and plated by a copper plating method of the present invention.

15 Semiconductor elements 46 are mounted on (the) predetermined locations of said multi-layer wiring board 54 by a method using solder balls 44. With this, a highly reliable module can be obtained.